The Application of Synchrotron X-Ray Fluorescence Microanalysis to Dendroanalysis: Detecting a Contaminant Signature in Salix Nigra Annual Rings

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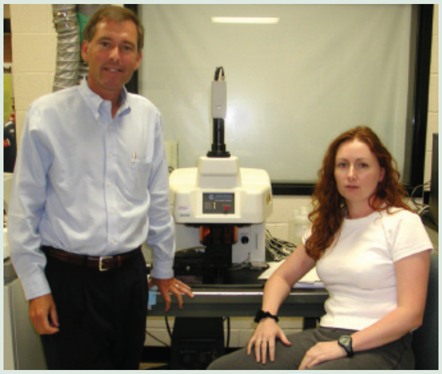
Synchrotron X-Ray Fluorescence microanalysis (SXRF) was used to test the accuracy of dendroanalytical data using willows (Salix nigra L.) collected from an eroding U- and Ni-contaminated former settling pond and the impacted area downstream. Increases in background Ni concentration and enrichment in specific annual rings were in good agreement with contaminant history. High resolution spatial analysis showed that ring boundaries sharply separated differentially enriched annual rings, and revealed both a discrete and diffuse Ni distribution thought to be consistent with Ni transport within and binding to vessel elements in woody tissue, respectively.



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Dendroanalysis, the measurement of the chemical composition of a tree's annual rings for retrospective biomonitoring, is a controversial area of study. For metals, the accuracy of the environmental record is based on the assumption that elemental distribution remains stable, however, reports of metal mobility have questioned this. Techniques capable of providing spatially-resolved elemental composition data, such as Synchrotron X-ray Fluorescence microanalysis (SXRF), can considerably enhance our understanding of metal transport and distribution within tree rings. In order to test the accuracy of dendroanalysis, annual rings from trees with a well-documented contaminant history, where metal concentrations have fluctuated in recent years, were investigated using SXRF at the dedicated microprobe beamline, X26A.

Steed Pond functioned as a de facto settling basin for uranium (U) and metal wastes discharged to a stream from a nuclear target and fuel fabrication facility on the Savannah River Site between 1954-1985, effectively retaining U (natural and depleted), Ni, Cu, Zn, and Al in its pond sediments. When the enclosing spillway breached in 1984, the water level fell and a pulse of contaminated sediments moved downstream, being redeposited in Lower Tims Branch; a process that continues during seasonal storms. We investigated whether willows collected from the contaminant source and sink areas, found to contain elevated metal concentrations in their leaves, contained the geochemical signature of contaminants in their annual rings.

Tree core samples were collected from Steed Pond and Lower Tims Branch, dated and analyzed using SXRF. One-dimensional line scans collected X-ray fluorescence data along the length of the core samples, from pith to cambium, to show changes in metal concentration throughout the lifetime of the trees. We found that samples from Steed Pond (source) contained higher concentrations of Ni than those collected from Lower Tims Branch (sink), indicating that SXRF can be used to provide quantitative data. Samples collected from Lower Tims Branch, pre-dating the spillway breach, clearly showed a large pulse in

Ni, Cu, and Zn in 1985, and again in 1991 (**Figure 1**), correlating with known contaminant pulses. In agreement with previous bioavailability studies, U was not detected in any of the samples.

Two-dimensional elemental maps of Ni closely resembled digital images of annual rings (**Figure 2**), and annual ring boundaries sharply separated differentially Ni-enriched zones. Elucidating this required a rigorous sample resolution and coverage, entailing a focused X-ray beam (10 × 15 μm) and small step size (30 μm); approximately 125,000 data points. Closer observation of the Ni-enriched ring revealed sporadically distributed, exclusively Ni-containing features, approximately 10-20 μm in diameter (**Figure 3**). Using the digital imaging capabilities at X26A, we could see this was a non-structural Ni-enriched substance within the lumen of vessel elements. Contrasting intense and diffuse Ni distributions may conceivably arise from Ni transport within and binding to annual rings, respectively, and are the subject of continued investigation using Size-Exclusion Chromatography and X-Ray Absorption Near Edge Spectroscopy (XANES).

This study demonstrates that micron-scale heterogeneity of metal distribution in the vascular system of woody plans can provide misleading data, but that the more rigorous two-dimensional elemental imaging obtainable with SXRF allows an accurate interpretation of dendroanalytical data with minimal sample preparation.

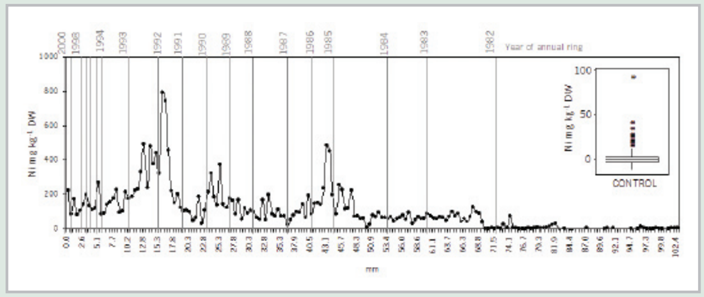

Figure 1. One-dimensional line scan of the Ni concentration (mg kg^{-1} d. wt) within annual rings of Salix nigra L. (black willow) collected from Lower Tims Branch referenced against the annual ring positions. Inset shows summarized control data.

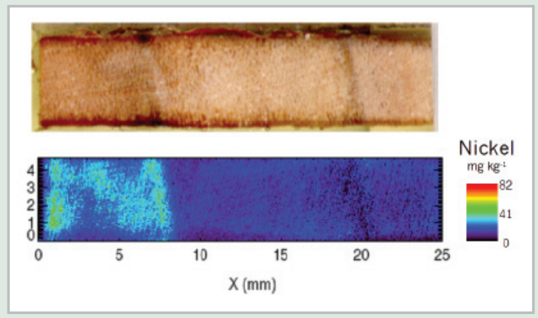

Figure 2. Digital photograph and compositional map of Ni fluorescence counts in the annual rings of Salix nigra L.

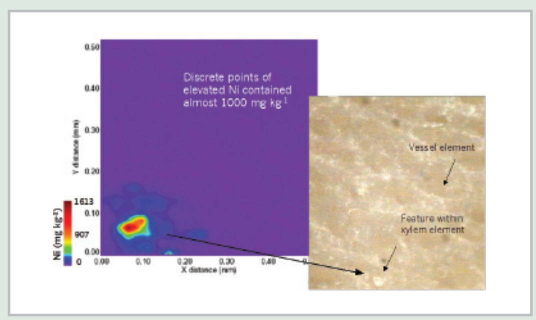

Figure 3. Discrete area of concentrated Ni distribution (shown as mg kg^{-1}), compared to digital photograph of the corresponding area, showing open ends of vessel elements and the location of the Ni feature.